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(54) Title: POLYISOCYANATE COMPOSITIONS

(57) Abstract

The invention provides organic polyisocyanate compositions comprising a polyisocyanate component and a non-ionic surface active agent devoid of isocyanate-reactive groups characterised in that the polyisocyanate component comprises an isocyanate-containing reaction product of a uretonimine-modified polyisocyanate and a polyol having a molecular weight of from 500 to 10,000. The invention further provides aqueous emulsions derived from the polyisocyanate compositions, a method of their use for binding polyurethane foam scrap and foam composites prepared by the method.

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POLYISOCYANATE COMPOSITIONS

This invention relates to polyisocyanate compositions and more particularly to water-emulsifiable polyisocyanate compositions, to methods for their preparation, to the derived aqueous emulsions and to the use of said emulsions as binders.

Organic polyisocyanate compositions which are emulsifiable in water are already known as is the use of the derived aqueous emulsions as binders and adhesives. Thus, in United Kingdom Patent Specifications Nos. 1,444,933 and 1,523,601, there are described emulsifiable polyisocyanate compositions comprising an organic isocyanate and a non-ionic surface active agent free of hydroxy, amino and carboxylic acid groups. Isocyanates which may be present in said compositions include aliphatic, cycloaliphatic and, especially, aromatic polyisocyanates and also isocyanate-ended prepolymers made by reaction of an excess of a polyisocyanate with a polyester or polyether polyol, a monomeric polyol or castor oil. The derived aqueous emulsions may be applied to wood chips and other ligno-cellulosic materials to produce particle boards and similar composite articles.

In order for the aqueous emulsions to have commercial utility, it is desirable that they should be stable for a period of several hours and, preferably, for several days.

Unfortunately, many of the known emulsifiable polyisocyanates have not been entirely satisfactory in this respect, the derived emulsions showing undesirable phase separation and/or reduction in isocyanate value after a relatively short period of time.

It has now been found that aqueous emulsions having improved stability may be obtained from emulsifiable polyisocyanates derived from prepolymers of uretonimine-modified polyisocyanates.

Thus, according to the invention, there is provided an organic polyisocyanate composition comprising a polyisocyanate component and a non-ionic surface active agent devoid of isocyanate-reactive groups characterised in that the polyisocyanate component comprises an isocyanate-containing reaction product of a uretonimine-modified polyisocyanate and a polyol having a molecular weight of from 500 to 10,000.

The isocyanate-containing reaction product (a prepolymer containing urethane and uretonimine groups) may be obtained by reacting a polyol with a stoichiometric excess of a uretonimine-modified polyisocyanate under conditions that have been fully described in the prior art for the preparation of urethane prepolymers. Reaction temperatures of from about 40° to about 90°C are generally suitable, the excess of uretonimine-modified polyisocyanate being such as to give a reaction product having an isocyanate (NCO) content in the

range from about 2 to about 25 % on a weight basis, preferably from about 11 to about 15 %

Polyols which may be used in making the isocyanate-containing prepolymer preferably have hydroxyl functionalities of from 2 to 4, diols and triols and mixtures thereof being preferred. Particularly suitable polyols include polyether polyols, for example polyoxy-propylene and poly(oxypropylene-oxyethylene) diols and triols and, especially hydroxyl-containing fatty acid esters such as castor oil and hydrogenated castor oil. Other polyols which may be used include hydroxyl-terminated polyesters, polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins and polysiloxanes. Mixtures of polyols may be used, for example mixtures of polyoxy-propylene polyols and castor oil.

Uretonimine-modified polyisocyanates which may be used in making the isocyanate-containing prepolymer, and methods for their preparation, have been fully described in the prior art. In general, uretonimine-modified polyisocyanates are obtained by contacting an organic polyisocyanate with a carbodiimid-isation catalyst (commonly a phosphorus compound) to form a carbodiimide-modified polyisocyanate which reacts with unreacted isocyanate groups forming a uretonimine-modified polyisocyanate. Suitable phosphorus-containing catalysts include alkyl esters of phosphoric, phosphonic, phosphinic, phosphorous and phosphinous acids and the corresponding amides,

phosphine oxides and the phospholidines and phospholenes described in United Kingdom Patent Specification No. 1,476,088. In a typical procedure, the organic polyisocyanate is heated with an effective amount of a carbodiimidisation catalyst so as to convert from 5 to 40 % of the isocyanate groups to carbodiimide groups, the reaction mixture then being cooled, the catalyst being deactivated if desired or necessary and reaction between carbodiimide and isocyanate groups being allowed to take place to form the uretonimine derivative, thereby resulting in 7.5 % to 60 %, and preferably 10 % to 40 % conversion of initially present isocyanate groups into uretonimine-modified form.

Organic polyisocyanates from which the uretonimine-modified polyisocyanates may be prepared include aliphatic, cyclo-aliphatic and araliphatic polyisocyanates, for example hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate and m- and p- tetramethylxylene diisocyanates. The preferred polyisocyanates, however, are the aromatic polyisocyanates, for example phenylene diisocyanates, 2,4-and 2,6-tolylene diisocyanates, 1,5-napthylene diisocyanate and especially the available isomers of diphenylmethane diisocyanate (MDI), that is to say 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate and mixtures thereof. Other suitable polyisocyanates include the mixtures of diphenylmethane diisocyanates with oligomeric tri- and higher polyisocyanates known in the art as crude or polymeric MDI.

If desired, the polyisocyanate component may contain other isocyanate species, for example any of the organic polyisocyanates mentioned above, in addition to the prepolymer derived from the uretonimine-modified polyisocyanate. One preferred polyisocyanate component comprises a mixture of polymeric MDI and a prepolymer obtained by reacting uretonimine-modified diphenylmethane diisocyanate with a polyoxypropylene polyol and/or castor oil.

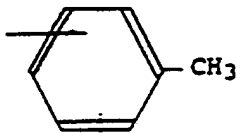
The non-ionic surface active agent devoid of isocyanate-reactive groups present in the compositions of the invention may be any of such agents described in the prior art. In particular, such agents include polyoxyalkylene, especially polyoxyethylene, compounds containing no free hydroxy, amino, carboxy or other isocyanate-reactive groups. These include, for example, condensates of alkylphenyls, long chain alcohols and amides with alkylene oxides, especially ethylene oxide, the terminal hydroxy group being etherified or esterified. Examples of such surface active agents have been described in the aforementioned United Kingdom Specifications 1,444,933 and 1,523,601 and in EP-A-0 019 844 and EP-A-0 095 594.

Of particular value are the reaction products of diisocyanates and higher functionality polyisocyanates with monoalkyl ethers of polyethylene glycols as described in United Kingdom Patent Specification No. 1,417,618. These particular surface active agents or emulsifying agents have the formula

$$RO(CH_2CH_2O)_nCONHX$$

wherein R is an alkyl group of from 1 to 4 carbon atoms, n is an integer such that the compound contains an average of at least 5 oxyethylene groups and X is the residue of a di- or polyisocyanate and contains at least one free isocyanate group. Examples of R include ethyl, propyl, butyl, and preferably methyl. It is preferred that n represents an average of from 5 to 120, and especially from 10 to 20.

The group X is the residue which would remain after one isocyanate group has been removed. The group X may be the residue of any diisocyanate or higher polyisocyanate and for example if the diisocyanate is a tolylene diisocyanate, the residue X will be



Isocyanates from which the group X can be derived include the di- and polyisocyanates listed above, the uretonimine-modified polyisocyanates made therefrom and the isocyanate-containing prepolymers derived from the uretonimine-modified polyisocyanates. Such surface active urethanes may be manufactured by reacting an alcohol of the formula

$$RO(CH_2CH_2O)_nH$$

wherein R and n have the same meaning as for the above described surface active or emulsifying agents, with an isocyanate having at least two isocyanate groups, there being used at least one molar proportion of isocyanate for each molar

proportion of the alcohol. Preferably an excess of the isocyanate is used.

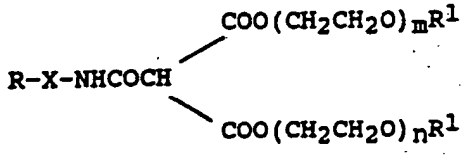
The reaction may be carried out by adding the alcohol to the isocyanate and allowing the reaction to proceed, preferably by heating the reaction mixture at a temperature of 50-150°C. Alternatively the reaction can be carried out at lower temperatures e.g. 25°C in the presence of a small amount of catalyst e.g. triethylenediamine.

In order to obtain emulsifiable polyisocyanates according to the present invention, the above type of surface active agent may be prepared in situ in the polyisocyanate component by reacting a small amount of the polyethylenoxy alcohol

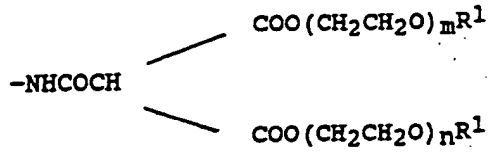
$$RO(CH_2CH_2O)_nH$$

with a large excess of that component.

A further type of surface active agent which may be utilised is that described in United Kingdom Patent Specification No. 1,417,276 which has the general formula



wherein X is the residue of an organic isocyanate, R^1 is an alkyl group of from 1 to 4 carbon atoms, n and m are integers such that m+n is at least 10 and R, which is only present when X represents the residue of a diisocyanate or a higher functionality polyisocyanate, is an isocyanate group or a group of the formula



R^1 is preferably methyl and the sum of m and n is preferably between 20 and 80.

X may for example be the residue of any of the isocyanates (including prepolymers) listed earlier in this specification.

These surface active agents or emulsifiers may be made by reaction of an isocyanate with a bis(alkoxy polyethylenoxy) ester of malonic acid, and may if desired be prepared in situ in the polyisocyanate component.
The amount of the non-ionic, surface-active agent in the polyisocyanate composition according to the present invention may range from 0.1 to 15 and preferably from 0.5 to 10 % by weight calculated on the whole composition.

From the polyisocyanate compositions according to the present invention aqueous emulsions can be made, said emulsions exhibiting an improved stability and pot-life. The emulsions may comprise 99 to 25 parts by weight of water and 1 to 75 parts by weight of the polyisocyanate composition according to the present invention. Preferably they comprise 70 to 50 parts by weight of water and 30 to 50 parts by weight of the polyisocyanate composition. Such emulsions are made by combining the polyisocyanate composition and the water while and/or followed by thoroughly mixing at ambient temperature.

The emulsions may further contain additives such as pigments, fillers, antioxidants, resins and plasticisers.

The emulsions are useful as adhesives, coatings, sizing-agents of paper and particularly as binders of lignocellulosic materials like woodchips and straw, in view of their excellent stability.

When the aqueous emulsions derived from the compositions of the invention are used as binders, known techniques may be employed, for example the techniques described in the afore-mentioned United Kingdom Specifications 1,444,933 and 1,523,601, EP-A-0 019 844 and EP-A-0 095 594.

The aqueous emulsions of the invention are also of particular value as binders for polyurethane foam scrap, especially flexible foam scrap which can be reconstituted for use as resilient backing for woven or tufted carpets. In a typical procedure, pieces of scrap foam are impregnated with the aqueous emulsion and the treated foam is compressed in a mould and injected with steam to promote cure.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

Example 1

A prepolymer having an NCO content of 13.7 % was prepared by reacting 62 parts of an isocyanate with a uretonimine content

of 16.4 % with 35 parts of castor oil and 3 parts of the monomethyl ether of polyethylene glycol having a molecular weight of 750.

A 30 % aqueous emulsion was prepared. The initial NCO content was measured and the change in NCO content then monitored during subsequent storage of the emulsion :

	NCO content	
Initial	4.1 %	
15 mins	3.6 %	
45 mins	3.2 %	Reduction of NCO content
100 mins	3.2 %	at 180 minutes = 27 % (interpolation)
300 mins	2.6 %	

Example 2

A prepolymer having an NCO content of 13.7 % was prepared as described in Example 1. A 47 % emulsion of the prepolymer in water, containing 5 % of butyl benzyl phthalate, was prepared. Initial and subsequent NCO contents were found to be as follows :

	NCO content	
Initial	6.1 %	
60 mins	6.1 %	Reduction of NCO content
120 mins	5.1 %	at 180 minutes = 15 % (extrapolation)

Emulsion stability was better than in Example 1.

Example 3

A prepolymer having an NCO content of 13.0 % was prepared by reacting 54 pts of an isocyanate having a uretonimine content of 16.4 % with 24.5 pts of castor oil, 8.5 pts of poly bdR-45HT, (a hydroxyl terminated polybutadiene resin with a molecular weight of 2500), 10 pts of butyl benzyl phthalate and 3 pts of the monomethyl ether of polyethylene glycol having a molecular weight of 750.

A 40 % aqueous emulsion was prepared. Initial and subsequent NCO contents were found to be as follows :

	NCO content	
Initial	5.2 %	
30 mins	4.8 %	Reduction of NCO content
200 mins	4.2 %	at 180 minutes = 21 % (interpolation)
1440 mins	1.0 %	

Example 4

A prepolymer having an NCO content of 12.8 % was prepared by reacting 54 pts of an isocyanate having a uretonimine content of 16.4 % with 24.5 pts of castor oil, 8.5 pts of Terathane 2000 (a polytetramethylene ether glycol of molecular weight 2000 : Terathane is a Registered Trade Mark), 10 pts of butyl benzyl phthalate and 3.0 pts of the monomethyl ether of polyethylene glycol having a molecular weight of 750.

A 40 % aqueous emulsion was prepared. Initial and subsequent NCO contents were found to be as follows :

	NCO content	
Initial	5.14 %	
25 mins	4.6 %	Reduction of NCO content
90 mins	4.2 %	at 180 minutes = 32 % (extrapolation)
160 mins	*3.6 %	

* product precipitating and foaming

Comparison Example 5

A prepolymer having an NCO content of 17.6 % was prepared by reacting 65.5 pts of Suprasec 1042 (a commercially available emulsifiable polyisocyanate containing no uretonimine-modified polyisocyanate components) with 34.5 pts of a 2000 molecular weight polypropylene glycol diol. (Suprasec is a Registered Trademark).

A 30 % aqueous emulsion was prepared. The initial and subsequent NCO contents were found to be as follows :

	NCO content	
Initial	5.3 %	
10 mins	4.8 %	Reduction of NCO content
30 mins	3.9 %	at 180 minutes = 93 %
45 mins	2.9 %	
180 mins	0.35 %	

Comparison of the reduction in NCO content on storage of an emulsion derived from a non-uretonimine modified emulsifiable polyisocyanate (Example 5) with those observed for emulsions prepared from polyisocyanates according to the invention shows a substantial improvement in pot-life for the invention compositions.

Aqueous emulsions derived from the invention compositions, when used as binders for foam scrap, yield foam composites having good properties, as shown in Table I. Properties of a foam composite derived from a standard toluene diisocyanate (TDI) prepolymer (TDI, 3000 molecular weight polypropylene glycol, triol and mineral oil) are reported in Table I for comparison purposes.

Table I - Properties of Foam Composites.

	Derived from Emulsion of Example 2			Derived from Emulsion of Example 3		Standard foam derived from TDI
Weight % Binder Level	4	5	6	5	6	6.5
Density (kg/m^3)	78	73	72	84	87	80
Tensile strength (N) (before lamination)	4.4	6.9	5.3	8.4	10.2	10.9
Work of compression- original (J/mm^2) (BS5808 App B)	169	169	163	144	150	134
After Dynamic loading	125	132	118	111	120	107
% loss	26.2	22	27.5	22.9	20.4	20.4
Comparison Original (mm)	6.9	6.7	7.1	6.3	6.0	6.5
After Dynamic loading (mm)	6.4	6.5	6.6	6.1	5.9	6.2
Thickness loss (%) (AS 2111.2)	8.6	5.7	8.2	6.1	5.8	6.0

CLAIMS

1. An organic polyisocyanate composition comprising a polyisocyanate component and a non-ionic surface active agent devoid of isocyanate-reactive groups characterised in that the polyisocyanate component comprises an isocyanate-containing reaction product of a uretonimine-modified polyisocyanate and a polyol having a molecular weight of from 500 to 10,000.

2. A composition according to claim 1 wherein the isocyanate content of the isocyanate-containing reaction product is in the range from 2 to 25 % by weight.

3. A composition according to claim 1 wherein the uretonimine content of the uretonimine-modified polyisocyanate is derived from conversion into uretonimine-modified form of 7.5 % to 60 % of the isocyanate group present in the unmodified polyisocyanate.

4. A composition according to claim 1 wherein the amount of non-ionic surface active ingredient is from 0.1 % to 15 % by weight calculated on the total composition.

5. A composition according to any one of claims 1-4 wherein the polyisocyanate component comprises an isocyanate-

containing reaction product of a uretonimine-modified polyisocyanate and a polyoxypropylene or poly(oxypropylene-oxyethylene) diol or triol, or a hydroxyl-containing fatty acid ester, or a mixture thereof.

6. A composition according to any one of claims 1 to 4 wherein the uretonimine-modified polyisocyanate comprises a uretonimine-modified diphenylmethane diisocyanate.

7. A composition according to any one of claims 1 to 4 wherein the polyisocyanate component comprises a mixture of polymeric MDI and a prepolymer obtained by reacting a uretonimine-modified diphenylmethane diisocyanate with a polyoxypropylene polyol and/or castor oil.

8. A composition according to any one of claims 1 to 4 wherein the non-ionic surface active agent is a compound of the formula :

$$RO(CH_2CH_2O)_nCONHX$$

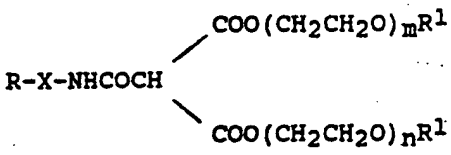
wherein R is a C_{1-4} alkyl group, n is an integer such that the compound contains an average of at least 5 oxyethylene groups and X is the residue remaining after removal of an isocyanate group from an organic polyisocyanate.

9. A composition according to claim 8 which is the product of reacting a polyethylenoxy alcohol of the formula :

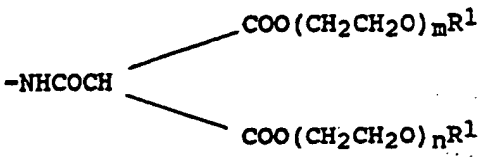
$$RO(CH_2CH_2O)_nH$$

wherein n is as defined in claim 8 with a large excess of a polyisocyanate component comprising an isocyanate-containing reaction product of a uretonimine-modified polyisocyanate and a polyol having a molecular weight of from 500 to 10,000.

10. A composition according to any one of claims 1 to 4 wherein the non-ionic surface active agent is a compound of the formula :



wherein X is the residue of an organic isocyanate, R^1 is an alkyl group of from 1 to 4 carbon atoms, n and m are integers such that m+n is at least 10 and R, which is only present when X represents the residue of a diisocyanate or a higher functionality polyisocyanate, is an isocyanate group or a group of the formula



11. An aqueous emulsion comprising water and an organic polyisocyanate composition according to any one of claims 1 to 4.

12. An aqueous emulsion according to claim 11 comprising from 99 to 25 parts by weight of water and from 1 to 75 parts by weight of the organic polyisocyanate composition.

13. A method for bonding together polyurethane foam scrap which comprises impregnating the foam scrap with an aqueous emulsion according to claim 11 and compressing the treated scrap.

14. A foam composite prepared according to method of claim 13.

15. A process for the preparation of a composition according to claim 9 which comprises reacting a polyethylenoxy alcohol of formula

$$RO(CH_2CH_2O)_nH$$

wherein n is an integer such that the compound contains an average of at least 5 oxyethylene groups, with a large excess of a polyisocyanate component comprising an isocyanate-containing reaction product of a uretonimine-modified polyisocyanate and a polyol having a molecular weight of 500 to 10,000.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/01452

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[5]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 G 18/79, C 08 L 75/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 G; C 08 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	EP, A1, 0309113 (ICI AMERICAS INC) 29 March 1989, see page 2, line 28 - line 29; page 3, line 5 - line 9; page 6, line 23 - line 34; claims 1,2	1-15
Y	GB, A, 1444933 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 4 August 1976, see page 3, line 10 - line 13; claims 1-12	1-15
Y	GB, A, 1523601 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 6 September 1978, see claims 1-22	1-15

* Special categories of cited documents:[10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
27th October 1992	11 NOV 1992
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Jack Hedlund

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A1, 0013487 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 23 July 1980, see the whole document	1-15
A	EP, A1, 0293088 (IMPERIAL CHEMICAL INDUSTRIES PLC) 30 November 1988, see the whole document	1-15

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/GB 92/01452

SA 62931

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/09/92
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0309113	29/03/89	JP-A-	1168756	04/07/89
		US-A-	4927876	22/05/90
GB-A- 1444933	04/08/76	SE-B-C-	402216	26/06/78
		SE-B-C-	421269	14/12/81
GB-A- 1523601	06/09/78	AU-D-	1195776	22/09/77
		BE-A-	839546	13/09/76
		CA-A-	1087825	21/10/80
		CH-A-	619975	31/10/80
		DE-A-B-C	2610552	23/09/76
		FR-A-B-	2303661	08/10/76
		LU-A-	74550	06/05/77
		NL-A-	7602614	14/09/76
		SE-B-C-	418271	18/05/81
		SE-A-	7603228	13/09/76
EP-A1- 0013487	23/07/80	US-A-	4448938	15/05/84
EP-A1- 0293088	30/11/88	AU-B-	596298	26/04/90
		AU-D-	1567488	01/12/88
		JP-A-	63309564	16/12/88
		US-A-	4892897	09/01/90